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Methylaluminoxane as an Alternative for BArF in the Iridium-Catalyzed Asymmetric Hydrogenation of Imines

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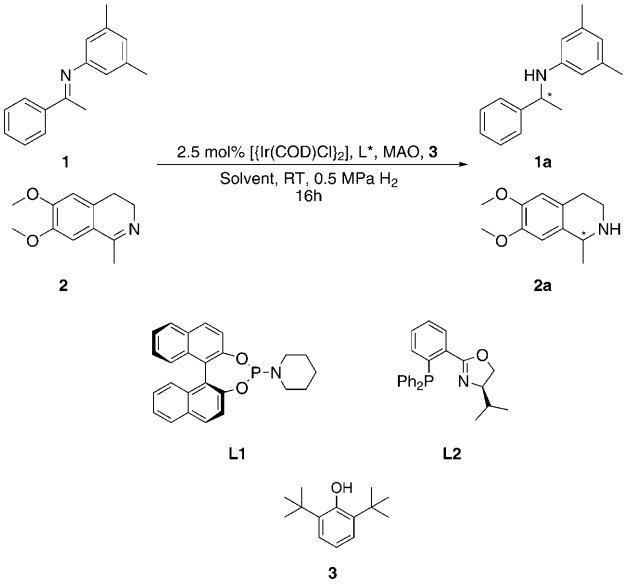
One of the methods for the preparation of enantiopure secondary amines is the asymmetric hydrogenation of imines. Over the last two decades, chiral catalysts based on iridium, rhodium, ruthenium, palladium, and titanium have been reported to be effective in the hydrogenation of C=N functionalities.[1]

Recently, we have published our results on the asymmetric hydrogenation of *N*-aryl imines using an iridium catalyst based on the use of the phosphoramidite ligand PipPhos **L1** and the BArF counterion.[2] In the hydrogenation of *N*-(3,5-dimethylphenyl)-(1-phenyl-ethylidene)-amine **1**, full conversion over 4 h and >99% *ee* was achieved. Using a catalyst precursor that contained chloride as counter ion, the reaction was much slower and needed higher temperatures and higher pressures to reach full conversion. In addition, the product was isolated with lower enantioselectivity. This underscores the importance of BArF as counter ion in this type of asymmetric hydrogenation.[3] In many hydrogenations the BArF counterion outperformed the PF_6 counterion, which is attributed to its steric bulk.[3c]

Phosphoramidites are cheap ligands that are easily made in only two synthetic steps.[4] They have found many applications in asymmetric hydrogenation.[5] However, the BArF counter ion is very expensive, which could hinder the industrial application of imine hydrogenation with Ir/PipPhos.

In olefin polymerization, the common metallocene halide catalysts are made cationic by reaction with a large excess of methylaluminoxane (MAO).[5] MAO is a poorly-defined oligomeric material roughly characterized by the formula $(Al(CH_3)_xO_y)_n$. MAO alkylates and then activates the metal-chloride pre-catalyst species by abstracting the chloride, thus forming an ion pair. It is prepared by a controlled hydrolysis of trimethylaluminium (TMA) and it always contains small amounts of TMA. TMA is a methylating agent and for that reason it is often removed by reaction with a bulky phenol, with which it forms $AlMe(OAr)_2$. Although a large excess of MAO is necessary in these polymerizations, the low cost and the innocuous nature of this compound makes this procedure very attractive as a potential replacement of BArF in asymmetric hydrogenation reactions. In addition, in view of its oligomeric nature MAO can be viewed as a "bulky" anion.

For these reasons the use of MAO was explored in combination with an iridium chloride catalyst precursor in the asymmetric hydrogenation of imines using PipPhos (**L1**) and the phosphine-oxazoline **L2**[3b,6] developed by Pfaltz as ligands (Scheme 1). Two imine substrates were chosen, *N*-aryl imine **1** and cyclic imine **2**. The hydrogenations were performed using



Scheme 1. Iridium catalyzed asymmetric hydrogenation of **1** and **2** using MAO as a counterion.

2.5 mol% of $[\{Ir(COD)Cl\}_2]$ at room temperature and 0.5 MPa of hydrogen pressure. Two different ligands were used, phosphoramidite (*S*)-PipPhos **L1** and commercially available phosphinooxazoline ligand **L2**. To remove traces of TMA from MAO, bulky phenol **3** was used in half of the experiments.

Two different concentrations of the MAO solution were employed and three different amounts were screened (5, 50, and 500 equivalents with respect to $[\{Ir(COD)Cl\}_2]$). Catalysts were prepared in a glovebox and the hydrogenation was performed at 0.5 MPa H_2 pressure in a Premex 96-Multi Reactor (96 reaction vessels). Solutions of MAO were dispersed by a liquid dispensing robot into the vials, optionally followed by the addition of a solution of the bulky phenol **3**. The substrate solution was then added, followed by the addition of the catalyst (pre-

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mixed solution of [{Ir(COD)Cl}$_2$] and ligand). Hydrogenation was carried out over 16 h.

Using 5 equivalents of MAO, with respect to the metal precursor, modest conversions were achieved suggesting that the dehalogenation of the iridium catalyst was not complete. However, when 50 equivalents of MAO were used, high conversions were achieved with both substrates (Table 1). Although no duplicates were performed, we see a good correlation between the results with MAO A (1.5 M in toluene) and MAO B (2.3 M in hexane), which differ only in the nature of the solvent, particularly when phenol **3** was used. High enantioselectivity was achieved in the hydrogenation of *N*-aryl imine **1** using phosphinooxazoline **L2** in dichloromethane, without the use of phenol (98% yield, 76% *ee*). The same substrate was hydrogenated in the presence of PipPhos (**L1**) and phenol in toluene with up to 45% *ee* in 98% yield. In the case of dihydroisoquinoline **2**, the best result was achieved by using PipPhos **L1** and phenol in toluene (87% yield, 32% *ee*). When ligand **L2** was employed on the same substrate, without phenol in toluene, only 12% yield and 24% *ee* was reached.

Using 500 equivalents of MAO, yields of the desired product were mostly very low, especially of the cyclic imine **2** (Table 2). In the cases where there was no product observed, the starting material was also decomposed. This is particularly prevalent in the absence of **3**. Thus we assume that with these large amounts of MAO methylation of the imines occurs. The highest enantioselectivity was obtained in the hydrogenation of *N*-aryl imine **1** using phosphinooxazoline ligand **L2** in dichloromethane, without the presence of phenol (89% *ee*, 40% conversion). In the hydrogenation of the same substrate using **L1** the best result was achieved by using dichloromethane and in the presence of **3** (35% *ee*, 82% conv.) Dihydroisoquinoline **2** was hydrogenated with up to 84% *ee* (70% conversion) in dichloromethane with ligand **L2**, with addition of **3**. The use of **L1** in the hydrogenation of the cyclic imine **2** led to formation of **2a** in 47% yield and 47% *ee* in the presence of **3**.

To gather experimental evidence for the cationic nature of the iridium complex after addition of MAO, we first treated [{Ir(COD)Cl}$_2$] with 2 equiv of **L2** in $CDCl_3$ to obtain a single complex for which we assume structure **A**. The ^{31}P NMR spectra of the neutral complex **A** showed a single peak at $\delta =$ 15.8 ppm. Treatment of **A** with 50 equiv of MAO in toluene gave a new complex which we assume to be the cationic square planar complex **B** (Scheme 2). This complex also showed a single peak in the ^{31}P NMR spectra at $\delta = 17.4$ ppm. This compares very well with the [Ir(**L2**)(COD)]BArF complex, to which the peak at $\delta = 17.2$ ppm is attributed. Even more significant, were the changes in the ^{1}H NMR spectra. Whereas complex **A** shows two broad absorptions

Table 1. Asymmetric hydrogenation of imines using iridium catalysts and 50 equivalents of MAO.[a,b]

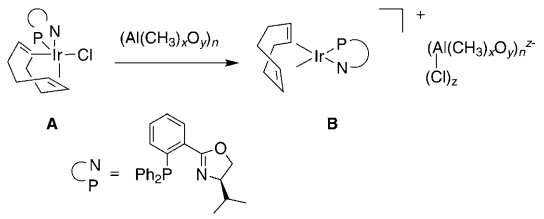
Yield of amine[c] [%]			50 Equivalents			
			MAO A		MAO B	
Phenol	Solvent	Substrate	Ir/**L1**	Ir/**L2**	Ir/**L1**	Ir/**L2**
with **3**	CH_2Cl_2	**1**	98	98	99	99
	CH_2Cl_2	**2**	85	20	95	19
	toluene	**1**	98	98	98	98
	toluene	**2**	74	12	87	9
without **3**	CH_2Cl_2	**1**	98	98	99	5
	CH_2Cl_2	**2**	95	15	97	12
	toluene	**1**	–	98	81	99
	toluene	**2**	11	5	94	12
Selectivity *ee*[d] [%]			50 Equivalents			
			MAO A		MAO B	
Phenol	Solvent	Substrate	Ir/**L1**	Ir/**L2**	Ir/**L1**	Ir/**L2**
with **3**	CH_2Cl_2	**1**	40	60	40	66
	CH_2Cl_2	**2**	30	12	26	16
	toluene	**1**	38	48	**45**	57
	toluene	**2**	6	14	**32**	−10
without **3**	CH_2Cl_2	**1**	18	**76**	37	–
	CH_2Cl_2	**2**	15	−10	14	15
	toluene	**1**	–	59	42	70
	toluene	**2**	−27	12	4	**24**

[a] Reaction conditions: 100 μmol imine, 2.5 μmol [{Ir(COD)Cl}$_2$], 10 μmol (*S*)-PipPhos **L1**, 125 μmol MAO, 250 μmol phenol **3**, solvent, RT, 0.5 MPa H_2, 16 h. [b] 100 μmol imine, 2.5 μmol [{Ir(COD)Cl}$_2$], 5 μmol **L2**, 125 μmol MAO, 250 μmol phenol **3**, 2.45 mL of solvent, RT, 0.5 MPa H_2, 16 h. [c] Yield was determined by GC and HPLC. [d] Enantiomeric excess was determined by HPLC.[e]MAO A = 1.5 M in toluene, MAO B = 2.3 M in heptane.

Table 2. Asymmetric hydrogenation of imines using iridium catalysts and 500 equivalents of MAO.[a,b]

Yield of amine[c] [%]			500 Equivalents			
			MAO A		MAO B	
Phenol	Solvent	Substrate	Ir/**L1**	Ir/**L2**	Ir/**L1**	Ir/**L2**
with **3**	CH_2Cl_2	**1**	82	81	94	95
	CH_2Cl_2	**2**	0	0	47	70
	toluene	**1**	82	83	95	94
	toluene	**2**	0	0	0	32
without **3**	CH_2Cl_2	**1**	3	2	13	40
	CH_2Cl_2	**2**	0	0	0	0
	toluene	**1**	5	3	17	48
	toluene	**2**	0	0	0	0
Selectivity *ee*[d] [%]			500 equivalents			
			MAO A		MAO B	
Phenol	Solvent	Substrate	Ir/**L1**	Ir/**L2**	Ir/**L1**	Ir/**L2**
with **3**	CH_2Cl_2	**1**	**35**	15	30	60
	CH_2Cl_2	**2**	–	–	**47**	**84**
	toluene	**1**	11	21	5	51
	toluene	**2**	–	–	–	66
without **3**	CH_2Cl_2	**1**	–	–	–	**89**
	CH_2Cl_2	**2**	–	–	–	–
	toluene	**1**	–	–	–	65
	toluene	**2**	–	–	–	–

[a] Reaction conditions: 100 μmol imine, 2.5 μmol [{Ir(COD)Cl}$_2$], 10 μmol (*S*)-PipPhos **L1**, 1250 μmol MAO, 2500 μmol phenol **3**, solvent, RT, 0.5 MPa H_2, 16 h. [b] 100 μmol imine, 2.5 μmol [{Ir(COD)Cl}$_2$], 5 μmol **L2**, 1250 μmol MAO, 2500 μmol phenol **3**, 2.45 mL of solvent, RT, 0.5 MPa H_2, 16 h. [c] Yield was determined by GC and HPLC. [d] Enantiomeric excess was determined by HPLC. [e] MAO A = 1.5 M in toluene, MAO B = 2.3 M in heptane.



Scheme 2. Formation of cationic square planar iridium complex upon treatment of the neutral complex **A** with MAO.

for the olefinic COD protons at $\delta = 4.04$ and 3.85 ppm, in complex **B** all 4 vinylic protons show separate resonances at $\delta =$ 5.27, 5.15, 3.55, and 3.35 ppm. This again, compares very well with the BArF complex for which these absorptions are at $\delta =$ 5.13, 5.02, 3.40, and 3.13 ppm, confirming that both are square planar complexes. In addition, the resonance for the proton at C-4 of the oxazolidine moves from $\delta = 4.60$ ppm in **A** to $\delta =$ 4.50 ppm in **B**, whereas in the BArF complex this is $\delta =$ 4.45 ppm.

Analysis of these results reveals that MAO is an interesting substitute for the expensive BArF counterion in the asymmetric hydrogenation of imines although the ratio of MAO to iridium needs careful adjustment. In the present case 50 equivalents gave the best results in terms of rate, but more work is needed to establish the true optimum ratio. It is clear that in industrial applications, the iridium catalyst will be used at less than 0.1 mol%, which translates to a mere 5 mol% of MAO. The rate of the hydrogenation with 50 equivalents is somewhat lower than the rate obtained in the BArF reaction; however, it is much faster than using the chloride precursor without MAO. The enantioselectivity of the reaction is clearly influenced as well. Here, apparently the enantioselectivity increases with increasing amount of MAO. In the hydrogenation of substrate **1**, 99% *ee* was previously obtained by using Iridium, BArF, and PipPhos. Here we achieved a maximum of 89% *ee*. Nevertheless, these are only preliminary results that show the potential of the method. It is possible to test more variants of MAO and indeed many modified forms of MAO and several smaller model compounds have been reported.[6b] It may also be possible to use other hydrolyzed trialkylaluminum compounds. In this context we would also like to draw attention to the work of Leitner and co-workers, who showed that in the nickel-catalyzed hydrovinylation reaction BArF can be replaced by using a combination of a halide containing pre-catalyst and a Lewis acid. In particular indium and bismuth based Lewis acids led to the formation of highly reactive catalysts.[8]

In conclusion, methylaluminoxane was shown to be an efficient substitute for the expensive BArF counterion in iridium-catalyzed asymmetric imine hydrogenation although the rate of the reaction and the enantioselectivity were somewhat lower than those obtained with BArF as counterion. We expect that this low-cost technology will open the way to more industrial applications of iridium-catalyzed asymmetric hydrogenation.

Experimental Section

Solvents were anhydrous and were purchased from Fluka and Aldrich. Dihydroisoquinoline **2** was purchased from Acros and used without purification. Metal precursor [{Ir(COD)Cl}$_2$] was purchased from Strem, whereas ligand **L2** was purchased from Fluka. Ligand **L1** was prepared according to the literature procedure.[9]

High throughput hydrogenations were performed in a Premex 96 autoclave. NMR spectra were measured by using Varian Gemini-200 and Varian AMX400 spectrometers. GC analysis was performed by using a HP6890 with a flame ionization detector (Agilent HP-5 column), whereas HPLC analysis was performed by using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector. The enantiomeric excess was determined by using Agilent HPLC with a chiral column (Chiralcel OD-H) in comparison with racemic products. Racemic amines were prepared by reduction of the imines with sodium borohydride in ethanol. High resolution mass spectra were recorded by using an AEI-MS-902 mass spectrometer. Optical rotations were measured by using a Schmidt+Haensch polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g per 100 mL).

General experimental procedure for the preparation of the imine **1**: A 100 mL round-bottom flask was filled with acetophenone (5.8 mL, 50 mmol) and 3,5-dimethylaniline (7.5 mL, 60 mmol) and molecular sieves (4 Å, 20 g) in toluene (30 mL). The reaction mixture was stirred at room temperature overnight, filtered and the solvent evaporated. The crude product was purified by Kugelrohr distillation.

General procedure for the hydrogenation experiments with the use of MAO as a counterion: Reactions were performed using 2.5 mol% of [{Ir(COD)Cl}$_2$] (2.5 μmol, 1.67 mg) at room temperature and 0.5 MPa of hydrogen pressure. PipPhos **L1** (10 μmol, 3.99 mg) and [{Ir(COD)Cl}$_2$] (2.5 μmol, 1.67 mg) were dissolved in solvent (200 μmol) and pipetted into each vial. Phosphinooxazoline ligand **L2** (5 μmol, 1.86 mg) and [{Ir(COD)Cl}$_2$] (2.5 μmol, 1.67 mg) were dissolved in solvent (200 μmol) and pipetted into each vial.

For 5 equiv of MAO: Phenol **3** (25 μmol, 5.51 mg, per reaction vial), added as a solution in DCM or toluene (100 μL, 0.055 M). MAO A (1.5 M in toluene): 300 μL of MAO A was diluted with 3.30 mL of heptane. 100 μL of solution was pipetted per reaction vial. MAO B (2.3 M in heptane): 200 μL of MAO B diluted with 3.68 mL of heptane. 100 μL of solution was pipetted per each reaction vial.

For 50 equiv of MAO: Phenol **3** (250 μmol, 55.1 mg per reaction vial), added as a solution in DCM or toluene (100 μL, 0.055 M). MAO A (1.5 M in toluene): 83 μL of solution was pipetted per each reaction vial. MAO B (2.3 M in heptane): 54 μL of solution was pipetted per each reaction vial.

For 500 equiv of MAO: Phenol **3** (2.5 mmol, 551 mg per reaction vial), added as a solid. MAO A (1.5 M in toluene): 833 μL of solution was pipetted per each reaction vial. MAO B (2.3 M in heptane): 544 μL of solution was pipetted per each reaction vial.

Substrates were added as a solution in DCM or toluene (100 μmol of substrate, 2.25 mL of solvent). Solutions were pipetted in a glovebox and the hydrogenation was performed in the Premex 96-Multi Reactor with 96 reaction vessels. Solutions of MAO were dispensed by using a liquid dispensing robot (Zinnser's Lizzy) into the vials, following by the addition of the phenol (**3**) solution. The substrate solution was then added, followed by the addition of the catalyst (pre-mixed solution of [{Ir(COD)Cl}$_2$] and ligand). Hydrogenation was performed over 16 h at 0.5 MPa.

N-(3,5-Dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (**1**)[10]: Yellow oil, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.25$ (s, 3H), 2.34 (s, 6H), 6.44 (s, 2H), 6.75 (s, 1H), 7.44–7.48 (m, 3H), 7.96–8.0 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.3$, 22.3, 117.9, 125.8, 128.1, 129.3, 131.3, 139.5, 140.6, 152.7, 165.9 ppm; HRMS calcd. for $C_{16}H_{17}N$ [*M*+1]: 223.1361; found: 223.1359.

(*R*)-*N*-(3,5-Dimethyl-phenyl)-(1-phenyl-ethyl)-amine (**1a**)[11]: Yellow oil, 97% yield, >99% *ee*, $[\alpha]_D = +12.3$ ($c = 1.02$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.62$ (d, $J = 6.7$ Hz, 3H), 2.32 (s, 6H), 4.02 (br, 1H), 4.61 (q, $J = 6.7$ Hz, 1H), 6.31 (s, 2H), 6.47(s, 1H), 7.34–7.37 (m, 1H), 7.43–7.47 (m, 2H), 7.50–7.52 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.4$, 25.8, 54.2, 112.2, 120.2, 126.8, 127.7, 129.5, 139.6, 146.4, 148.3 ppm; HRMS calcd. for $C_{16}H_{19}N$ [*M*+1]: 225.1517; found: 225.1504. HPLC (OD-H, eluent: heptane/*i*PrOH = 90:10, detector: 215 nm, flow rate: 0.5 mL min^{-1}), $t_1 = 8.5$ min, $t_2 = 9.0$ min. Conversion was determined by using GC: Agilent HP-5, initial temp. 80 °C for 2 min, then 15 °C min^{-1} to 280 °C, hold 4 min, retention times: starting imine $t = 11.9$ min, product $t = 11.5$ min.

6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (**2a**)[12]: White solid, 98% yield, m.p. = 97.3–97.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.41$ (d, $J = 6.28$ Hz, 3H), 2.61–2.65 (m, 1H), 2.75–2.80 (m, 2H), 2.94–2.99 (m, 1H), 3.21–3.24 (m, 1H), 3.81 (s, 6H), 4.03 (br, 1H), 6.53 (s, 1H), 6.58 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 23.6, 30.2, 42.5, 52.0, 56.7, 56.9, 109.9, 112.6, 127.5, 133.0, 148.2, 148.3 ppm; HPLC (OD-H, eluent: heptane/*i*PrOH = 88:12, detector: 215 nm, flow rate: 0.5 mL min^{-1}), $t_1 = 23.5$ min, $t_2 = 28.3$ min.

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Keywords: asymmetric catalysis · hydrogenation · imines · iridium · methylaluminoxane

[1] a) N. Fleury-Brégeot, V. de La Fuente, S. Castillón, C. Claver, *ChemCatChem* **2010**, *2*, 1346–1371; b) F. Spindler, H.-U. Blaser in *Handbook of Homogeneous Hydrogenation, Vol. 3* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH: Weinheim, **2007**, Chap. 34, pp. 1193–1215; c) P. Roszkowski, Z. Czarnocki, *Mini-Rev. Org. Chem.* **2007**, *4*, 190–200; d) W. Tang, X. Zhang, *Chem. Rev.* **2003**, *103*, 3029–3070; e) H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103–151; f) H.-U. Blaser, F. Spindler, *Comprehensive Asymmetric Catalysis, Vol. 1* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto, Springer, Berlin, **1999**, pp. 247–265.

[2] N. Mršić, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *J. Am. Chem. Soc.* **2009**, *131*, 8358–8359.

[3] a) H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600–2604; b) A. Lightfoot, P. Schnider, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 3047–3050; *Angew. Chem. Int. Ed.* **1998**, *37*, 2897–2899; c) S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, *J. Am. Chem. Soc.* **1999**, *121*, 6421–6429.

[4] a) Houben-Weyl, *Methoden der Organischen Chemie, Vol. XII/2* (Ed.: E. Müller), Thieme, Stuttgart, **1964**, pp. 99; b) R. S. Edmundson in *Comprehensive Organic Chemistry, Vol. 2, Part 10.3* (Eds.: D. H. R. Barton, W. D. Ollis), Pergamon Press, Oxford, **1979**; c) A. van Rooy, D. Burgers, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 492–498; d) A. H. M. de Vries, A. Meetsma, B. L. Feringa, *Angew. Chem.* **1996**, *108*, 2526–2528; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2374–2376; e) R. Hulst, N. K. de Vries, B. L. Feringa, *Tetrahedron: Asymmetry* **1994**, *5*, 699–708.

[5] a) M. van den Berg, A. J. Minnaard, E. P. Schudde, J. van Esch, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *J. Am. Chem. Soc.* **2000**, *122*, 11539–11540; b) M. van den Berg, A. J. Minnaard, R. M. Haak, R. Leeman, E. P. Schudde, A. Meetsma, B. L. Feringa, A. H. M. de Vries, C. E. P. Maljaars, C. E. Willans, D. Hyett, J. A. F. Boogers, H. J. W. Henderickx, J. G. de Vries, *Adv. Synth. Catal.* **2003**, *345*, 308–323; c) H. Bernsmann, M. van den Berg, R. Hoen, A. J. Minnaard, G. Mehler, M. T. Reetz, J. G. de Vries, B. L. Feringa, *J. Org. Chem.* **2005**, *70*, 943–951; d) A. J. Minnaard, B. L. Feringa, L. Lefort and J. G. de Vries, *Acc. Chem. Res.* **2007**, *40*, 1267–1277.

[6] a) G. Fink in *Handbook of Heterogeneous Catalysis (2nd Edition)*, Vol. 8, (Eds: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3792–3830; b) E. Y. X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434.

[7] P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger, A. Pfaltz, *Chem. Eur. J.* **1997**, *3*, 887–892.

[8] N. Lassauque, G. Franciò, W. Leitner, *Eur. J. Org. Chem.* **2009**, 3199–3202.

[9] L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* **2000**, *56*, 2865–2878.

[10] M. N. Cheemala, P. Knochel, *Org. Lett.* **2007**, *9*, 3089–3092.

[11] F. Y. Kwong, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 793–796.

[12] B. T. Cho, S. K. Kang, *Tetrahedron* **2005**, *61*, 5725–5734.

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